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THE CHEMICAL RELATION OF IRON AND MANGANESE IN SEDIMENTARY ROCKS.

IRON and manganese are frequent constituents of sedimentary rocks, in some places occurring finely disseminated through sandstones and shales, or forming a part of limestones, in other places forming the mass of the deposit in which they occur. They are both derived primarily from similar, and often from the same sources, and are in many respects alike in their chemical behavior in nature. For these reasons it is to be expected that they would frequently, if not generally, be deposited in intimate association. Such is found to be the case, and iron and manganese are often closely associated in the same deposits. Very often, however, iron and manganese deposits occur close together, but distinctly separated, while sometimes extensive deposits of iron, and less commonly of manganese, occur with little or almost no association with each other.

It is the object of the present paper to discuss the agencies which are instrumental in causing these substances to be deposited sometimes together and at other times separately. The subject is of interest as showing how slight differences in the chemical behavior of their salts may cause the almost complete separation of metals once intimately associated.

THE CONNECTION OF IRON AND MANGANESE IN NATURE.

A few words concerning the relation of manganese to iron in nature will perhaps make the following discussion clearer. One of the most common modes of occurrence of manganese is with iron, though extensive deposits containing manganese more or less free from iron often occur. When associated with iron, manganese occurs with it in various ways. Sometimes the two are intimately mixed, so that they have the appearance of a homoge-

neous mass, resembling iron ore when iron is in the preponderance and manganese ore when manganese predominates. In such cases there appears to be no tendency to combine in one fixed proportion, though, as iron is a much more abundant substance than manganese, the mixture most commonly contains an excess of iron, and exists in the form of a manganiferous iron ore. The manganese, when not intimately mixed with the iron, may occur in it in pockets or as scattered nodules and concretions. Such occurrences as those described are frequent in the Lake Superior iron region, the Appalachian Valley of the eastern states, in Nova Scotia, Arkansas, Colorado, New Mexico and innumerable other places. In Virginia very common occurrences are alternating layers of iron and manganese ore. The iron in such cases is generally in the larger quantities and the more continuous deposits; while the manganese is often represented by thin lenticular layers or by bands of nodules.

From such cases, where iron predominates, there are all gradations in admixture, up to the rarer cases where manganese predominates. Frequently a given geologic horizon is characterized by both iron and manganese, though in one case it may contain only iron, in another only manganese, and in still another iron and manganese mixed in various proportions. A remarkable case of this is seen in the iron and manganese horizons immediately above, or a short distance above, the Paleozoic quartzite, on the east side of the Appalachian Valley, especially in the Valley of Virginia.¹ Here deposits of iron ore, of manganese ore, and of both ores mixed, are found at various points along the same geologic horizons. Similar alternations also occur in the Lower Silurian novaculites of the Ouachita Mountains of Arkansas,² in Cebolla Valley, in Gunnison county, Colorado,³ and in

¹ The exact age of the iron and manganese deposits here referred to is, in some cases, a little uncertain. Some may be Cambrian, others Silurian, but the exact determination of the age of the horizon is not a part of the present discussion. The matter has been discussed by the writer in *Geological Survey of Arkansas*, 1890, Vol. I., pp. 376-379.

² See *Geological Survey of Arkansas*, 1890, Vol. I., pp. 320-325.

³ See *Geological Survey of Arkansas*, 1890, Vol. I., pp. 456-457.

many other places. In many cases certain horizons are characterized over large areas by iron alone, and but little manganese, as is well seen in the Clinton formation and in the Tertiary iron-ore horizons of Arkansas and Texas; while, on the other hand, some areas of certain horizons contain considerable quantities of manganese and very little iron, as is seen in parts of the Marine limestone in New Brunswick and Nova Scôtia, and also in parts of the metamorphosed Cretaceous shales of California.

THE SOURCE OF IRON AND MANGANESE IN SEDIMENTARY ROCKS.

The iron and manganese contained in sedimentary strata may be considered as derived primarily from the decay of pre-existing rocks. Some of the later sedimentary rocks may have derived a part or all of their iron from older sedimentary rocks, which, in turn, had derived their iron and manganese from still older rocks. In this way the iron and manganese in a given geologic horizon may have formed a part of various older horizons before they reached their present resting place, but, in every case, their primary source can be traced back to the original materials from which sedimentary rocks were first formed. In certain cases the sea water has supplied a certain amount of iron and manganese to sedimentary rocks, but in such cases the sea water acts only as a carrier of these materials from the land areas or from submarine sources to the strata then forming.

THE TRANSPORTATION OF IRON AND MANGANESE IN NATURE.

The process that goes on in this interchange of iron and manganese from older to younger rocks is as follows:

(1) The conversion, by surface agencies, of the minerals containing iron and manganese into forms that can be taken into solution by surface waters.

(2) The solution of the iron and manganese in surface waters, acidulated with organic and sometimes inorganic acids, and their transportation in this form from the areas of older rocks to areas over which younger rocks are being deposited.

(3) Finally, the precipitation in one or more of several ways of the iron and manganese contained in solution.

The iron and manganese thus chemically precipitated may be deposited either with mechanical sediments, such as sand, clay etc., or without them. If the deposition of mechanical sediments is largely in excess of the precipitation of iron and manganese, the final products will be beds of ferruginous shale, sandstone, etc., common in many geologic horizons. If the precipitation of iron and manganese is in excess of the deposition of mechanical sediments, the resulting products are deposits of more or less pure iron and manganese ore. Between these two extremes there are all gradations in the admixture of the iron and manganese with mechanical sediments.

Frequently the iron and manganese which were originally finely disseminated through shale, sandstone, etc., are subsequently concentrated into bodies of comparatively pure ore, and very commonly this concentration takes place by a process of re-solution of the iron and manganese and re-deposition by replacement with limestone, or, more rarely, with some other material. The limestone or other material which thus acts as a precipitant is often in the same series of strata from which the iron and manganese were removed, and thus these two substances, which were once in a finely disseminated condition, may be converted into deposits of comparatively pure ore and yet remain in the same general series of strata in which they were originally deposited. A remarkable case of this is seen in the iron deposits of the Penokee series in Michigan and Wisconsin,¹ to be mentioned again on page 370. It has also been suggested by H. D. Rogers² that certain siderite deposits in the Coal Measures were formed by the conversion of finely disseminated sesquioxide of iron into carbonate of iron by organic matter, and the subsequent segregation of the carbonate as now found in layers and nodules.

The surface waters that carry the iron and manganese to the strata being deposited at a given time are sometimes derived

¹R. D. Irving and C. R. Van Hise, U. S. Geol. Survey, Tenth Ann. Report, 1888-1889, Vol. I, pp. 409-422.

²Geol. Survey of Penn., Vol. II, 1858, p. 739.

from areas in which iron predominates, sometimes from areas in which iron and manganese are both abundant, and sometimes, though rarely, on account of the scarcity of such regions, from areas in which manganese largely predominates over iron. If iron and manganese were always precipitated from these waters in similar chemical forms and under the same conditions, it would be expected that the strata deriving their iron and manganese from surface waters would contain those substances in the same relative proportions as they had existed in the rocks from which they were derived, and that they would be in an intimately mixed condition. Such is doubtless often the case, or at least approximately so; but it is also often the case that iron and manganese occur in separate deposits, yet in close proximity to each other and often alternating along the same horizon. Besides this, the two substances frequently form parts of the same deposit and yet are distinctly separate from each other. In such cases the question arises as to why the iron and manganese are not intimately mixed in the form of a manganiferous iron ore, as would be expected if they had been precipitated together. Moreover, deposits sometimes occur which are composed largely of manganese ore, with little or almost no iron, and when the source of the manganese is looked for, we often find that the rocks which probably supplied it contained both manganese and iron, and that the iron was present in a much larger proportion as regards the manganese than in the new deposit. Here again the question arises as to why the iron and manganese are not in the same relative proportions in the new deposit as they were in the rocks from which they were derived.

Four principal causes suggest themselves in explanation of this separation :

(1) It might be supposed that the deposits containing mostly iron and those containing mostly manganese received these constituents from waters derived from different sources, and carrying iron and manganese only in the proportions in which they deposited them. Under some conditions this explanation might suffice, but in many cases, such as when iron and manganese alternate

along the same geologic horizon, and yet in close proximity with each other, the explanation is entirely inadequate, for the deposits are too close to each other to have been formed from different supplies of surface waters.

(2) It might be supposed that the iron or the manganese had been leached out of a deposit of the mixed ores, leaving one free from the other and depositing the dissolved ore somewhere else. This explanation, except in special cases, also appears inadequate, because the reagents in surface waters, which dissolve iron and manganese, seem to affect both about equally, so that if one were dissolved, the other should be taken up in the same way. Doubtless small differences could be found in the behavior of the organic and inorganic compounds in surface waters towards iron and manganese minerals, but they would be small as compared with the more active reactions which go on.

(3) It might be supposed that a separation could be produced by secondary concentration such as segregation, replacement, etc. This has doubtless sometimes been the case, but where the concentrating action is not assisted by a difference in the chemical behavior of the two substances, the separation would only be on a small scale. Even in the case of concentration by replacement of limestone, if iron and manganese both acted in the same way during the replacement, it would be expected to find them deposited in an intimate mixture. Though this secondary concentration, therefore, unassisted by other agencies, would not produce all the results found in nature, yet, when it is thus assisted, it often plays an important part.

(4) The fourth, and what seems the most important, factor in the separation of iron and manganese, is that, though very often they are precipitated in the same form from the same solution, yet sometimes they are precipitated in different forms; and even when precipitated in the same form, the precipitation of one sometimes requires different conditions from the precipitation of the other. This fact will explain the alternate association and separation of iron and manganese, not only when no secondary concentration has gone on, but also in cases where

such concentration has taken place, such as in the replacement of limestone, etc.

It will now be attempted to show how the various degrees of association and separation of iron and manganese found in nature may be produced by different conditions during deposition.

THE FORMS OF IRON AND MANGANESE DEPOSITED AT ORDINARY TEMPERATURES.

The mineralogical forms in which iron and manganese are deposited from solution in nature at ordinary temperatures depend on the conditions of air and water, whether of an oxidizing or a reducing nature, and on the character of the associated organic and inorganic matter either in solution or on the floor of the sea, lagoon or bog in which the deposition occurs.¹ There are four principal methods by which iron and manganese are precipitated in nature from surface waters :

(1) By oxidation, as in the case of the precipitation of hydrous oxides and in the precipitation of the carbonate by the partial oxidation of more complex organic salts.²

(2) By reduction, as in the precipitation of sulphide of iron by the reduction of sulphate of iron.

(3) By gaseous or soluble precipitants, as in the precipitation of sulphide of iron by the action of sulphuretted hydrogen or a soluble sulphide on a soluble salt of iron, and as in other cases to be mentioned later.

(4) By replacement of carbonate of lime or some other substance. Different forms are precipitated by these different methods.

Iron at ordinary temperatures is usually deposited from solu-

¹The solutions may be precipitated, as already shown, either with or without admixture with mechanical sediments; and there are in nature all gradations from almost pure deposits of iron and manganese ore to beds of shale, sandstone, etc. stained with iron or manganese. Subsequent concentration frequently causes decided changes in the latter deposits (see p. 370).

²It has been suggested by A. A. Julien (Proceed. Amer. Assoc. Adv. Sci., Vol. XXVIII., 1879, p. 356) that in some cases the carbonates of iron and manganese may be only the fixed residue of organic compounds of more complex form once in solution in surface waters.

tion as the hydrous sesquioxide, the carbonate, the sulphide or the hydrous silicate of iron and potash known as glauconite. Manganese under similar conditions is deposited as the hydrous oxide¹ or as the carbonate, and possibly sometimes, though very rarely, as sulphide.

When solutions of organic or inorganic salts of iron and manganese are freely exposed to the action of air, as in shallow or rapidly moving streams, or in lakes and some bogs, they are quickly oxidized and both may be deposited as more or less hydrous oxides. In many bogs, however, the metals may be precipitated as hydrous oxide on the surface where oxidizing agencies predominate, but when these oxides sink and come into contact with decaying organic matter, free from the active oxidizing influences of the air, they may be reduced to carbonates.

The carbonates of iron and manganese may be precipitated when the solutions containing them are protected from oxidation by a reducing agent, such as decaying organic matter, or by being far removed from the air. Carbonate of manganese, however, is a much more stable compound than carbonate of iron, and the oxidizing conditions are often sufficiently strong to cause the deposition of iron as hydrous sesquioxide and not strong enough to change the manganese from its carbonate form. It is not uncommon, therefore, to have iron deposited in one place as hydrous sesquioxide, and manganese carried further on and deposited as carbonate, or even under special conditions deposited as carbonate with the hydrous sesquioxide of iron. Fresenius² has shown that the warm springs of Wiesbaden, which contain iron and manganese among their other mineral constituents, deposit iron in the form of hydrous sesquioxide, while manganese is carried on further in solution and deposited as carbonate. In this behavior, therefore, we have the first striking difference in the deposition of iron and manganese, and it will be further discussed later on.

¹ This oxide is generally in the form of the peroxide or the sesquioxide in a more or less hydrous condition.

² *Jahrb. des Vereins f. Naturkunde in Herz. Nassau*, Vol. VI., p. 160 (Bischof).

The sulphides of iron and manganese differ very much in their nature and mode of occurrence. Iron is frequently deposited as sulphide, but manganese rarely occurs in that form, and when it does it is always in very small quantities. Iron forms several sulphides in nature: pyrite (FeS_2), marcasite (FeS_2),¹ pyrrhotite ($\text{Fe}_{11}\text{S}_{12}$), troilite (FeS) and numerous other more complex compounds unnecessary to enumerate here. Pyrite is the commonest form of iron sulphide, and occurs in rocks of all ages, from Archean to Recent. It is formed in nature by the action of soluble sulphides or sulphuretted hydrogen on soluble salts of iron, and also by the reduction of sulphate of iron by organic matter or other reducing agents. Manganese forms two² sulphides, alabandite (MnS) and hauerite (MnS_2). Both minerals are very rare, and so unstable that they rapidly oxidize on exposure. Alabandite is the less rare form, and usually occurs as a subordinate constituent of certain metalliferous veins or allied deposits.

Though the sulphides of manganese are easily oxidized, they are not so unstable that, had they ever been formed in considerable quantities in sedimentary deposits, they would, even at considerable depths, have left no trace of their former presence. Moreover, the sulphide of manganese, as produced artificially,³ is soluble in certain organic acids, notably acetic, and, as the conditions for the deposition of sulphides of metals in sedimentary deposits generally require the presence of organic matter, it is not improbable that some of the acids given off by such matter would be capable of dissolving sulphide of manganese. Here, then, is one reason why manganese might not be deposited as sulphide under some conditions which would cause the precipitation of sulphide of iron. Moreover, the artificial formation of sulphide of manganese (alabandite) in the laboratory is brought

¹ Marcasite has the same composition as pyrite, but differs in crystalline form.

² Manganese also occurs in the mineral youngite, which contains lead, zinc, iron, manganese and sulphur, but the mineral is considered of doubtful homogeneity. (See System of Mineralogy, E. S. Dana, 1892).

³ When manganese is precipitated artificially as sulphide it is usually in the form of the monosulphide (MnS), in either a hydrous or an anhydrous form.

about most easily at high temperatures. It has also been noted that when manganese, in the form of the alloys spiegeleisen and ferro-manganese, is added to molten steel, it bodily removes a part of the sulphur; and it is thought by some metallurgists, that sulphide of manganese is formed and carried into the slag.

These and other indications of the more easy transition of manganese into the form of sulphide at high rather than at low temperatures afford another cause which might prevent sulphide of manganese from being formed in sedimentary deposits, for such deposits are usually laid down at ordinary temperatures. On the other hand, they also afford a cause which might lead to the deposition of the sulphide of manganese in certain metalliferous veins and other deposits, where the temperature at the time of deposition may have been high.

In many of the silver and lead deposits of the Rocky Mountains manganese oxides occur with the superficial oxidation products of the sulphides of other metals, and it has often been suggested that the manganese also was originally in the form of sulphide. This may be true in some cases, for alabandite has been found in a few metalliferous deposits in Colorado, Mexico, Germany, Peru and elsewhere, but in most cases, at least in the Rocky Mountains, when the level is reached at which the oxidized forms of lead, zinc, iron and other metals pass into sulphides, the manganese passes into carbonate or silicate, and remains in one or both of those forms to all depths that have been reached.

In the deposition of iron and manganese as sulphide, therefore, there is a most marked difference of behavior, and here again is a good cause for the separation of the two substances in sedimentary rocks, as will be more fully explained below.

Iron is often deposited in sedimentary formations as the hydrous silicate of iron and potash known as glauconite, and composes the mass of the large greensand beds common in Cretaceous and Tertiary strata; but manganese is not found in an exactly similar condition.¹ Here again, therefore, is an import-

¹ Manganese occurs in various hydro-silicates, but they do not appear to be deposited as sedimentary strata in the same manner as glauconite.

ant difference in the modes of deposition of iron and manganese, which also will be mentioned again.

It will thus be seen that while some of the forms in which iron and manganese are deposited are the same, others differ very widely, and even similar forms are often deposited under different conditions. It is doubtless to these various forms and conditions of deposition that the alternate association and separation of iron and manganese in nature are due.

CAUSES OF THE ASSOCIATION OF IRON AND MANGANESE.

The very frequent intimate association of iron and manganese in sedimentary rocks is what would be expected from a deposition as oxide or carbonate in basins such as coastal lagoons or bogs, where the waters moved very slowly, or not at all, for under such conditions, they are often deposited together.¹ Moreover, it is a well-known fact that isomorphous substances have a strong tendency to combine in a homogeneous mass, and to crystallize together in different proportions. Carbonate of iron and of manganese are isomorphous with each other, and this is hence a possible cause of the frequent intimacy of their association, such as is seen in almost all manganiferous spathic iron ores, whether these ores are formed by direct precipitation or by replacement of carbonate of lime. The oxidation of such a mixture would give the common form of an intimately combined iron and manganese ore.

Since there is usually more iron than manganese in the rocks from which both metals were originally derived, the surface waters draining from areas of such rocks usually contain the metals in a similar proportion. Hence, in cases where the deposition of the carbonates of both occurs at the same spot, the isomorphous carbonates derived from the solutions have a larger percentage of carbonate of iron than of carbonate of manganese, and the resulting oxides contain the two metals in the same

¹ If the water moved very slowly, the deposition would probably take place approximately in the same spot; if the waters moved more rapidly, the iron might be deposited in one place and the carbonate in another, in the way explained on page 363.

proportion, thus giving rise to the common low-manganese iron ores.

The hydrous oxides of iron and manganese, however, are not isomorphous,¹ and, therefore, when they are precipitated together, as in bog-deposits, the association is often much less intimate than in the cases just mentioned, and is simply due to the fact that, under certain conditions, the oxides of both metals are precipitated in the same place.

CAUSES OF THE SEPARATION OF IRON AND MANGANESE.

When iron and manganese ores occur in more or less separate deposits, it becomes necessary to suppose the action of influences different from those which cause the deposition of both together, and such influences are to be found in the different modes of precipitation, under certain conditions, of the two metals. It has been shown by Fresenius² that certain warm springs, on reaching the surface, first deposit hydrous sesquioxide of iron, and farther on carbonate of manganese. This not only points to the well-known fact that carbonate of iron is more easily oxidized than carbonate of manganese, but it also leads to the belief that the bicarbonate or other salt of iron in the water is more easily oxidized than the manganese salt.

An action somewhat similar to that described by Fresenius readily explains the occurrence of manganese sometimes in entirely separate deposits, sometimes in distinct but closely alternating deposits.³ Under certain conditions, if the waters from which the precipitation took place were moving, the iron and manganese, owing to the difference in oxidability, as stated above, would be laid down in different places, resulting in the formation of deposits of iron ore free from manganese, and manganese ore free from iron in different positions along the plane of the same geologic horizon. Such occurrences are often seen in the iron

¹ The hydrous oxides of iron are not crystalline.

² See p. 363.

³ Bischof suggests that the action described by Fresenius causes the separate deposition of iron and manganese; and also that it explains the occurrence of large deposits of manganese ore in regions where the iron ore contains least of that ingredient. (See *Elements of Chemistry and Phys. Geol.*, Vol. III., pp. 531-532.)

regions of the Appalachian Valley, where there are often found, in different places along the same belt, deposits of iron ore and deposits of manganese ore in positions similar with relation to the enclosing rocks.

These conditions of moving water might also cause the occurrence of the two ores in interstratified layers, as is sometimes the case. Such a condition would result if iron were deposited in a certain place at one time, and if, later, on account of some increased facility for oxidation, iron was deposited before it reached that place, and the manganese, being less easily precipitated, were carried on and laid down upon the first deposit of iron.

Suppose the metalliferous solutions to be confined in a shallow basin, or, at least, to pass through it so slowly that they become thoroughly oxidized. Under such conditions the deposition of iron and manganese would go on continuously, and so nearly on the same spot that a comparatively homogeneous manganiferous iron ore would be formed. If the supply of metalliferous solutions were not continuous, but were intermittent, as is sometimes the case in local basins, such as coastal lagoons, which are often dependent for their supply of water on the changes of season and the sudden fluctuations of weather, then interstratified layers of iron and manganese ore might be produced. The iron, becoming oxidized on the surface, sinks to the bottom, possibly in some cases to be converted there to the simple carbonate by organic matter. Further oxidation precipitates hydrous oxide or carbonate of manganese on top of the iron. A renewed supply of surface waters brings more solutions of iron and manganese, or else the evaporation of the water in the closed basin concentrates the materials which have not yet been precipitated. In either case there is a further alternate deposition of the two ores.¹

Another process of separation of iron and manganese in nature might take place by the formation of sulphide of iron. It has already been shown that iron is sometimes deposited as sulphide and later oxidized in the same manner as the carbonate.

¹ In some cases these iron and manganese deposits are undoubtedly formed by the replacement of limestone or other rocks, as is further discussed on pages — to —.

Manganese, on the other hand, is rarely found as sulphide, and there is reason to think that the sulphide never represented the original form of any large sedimentary deposits of manganese ore (see pages 364 to 365). It seems probable, therefore, that from a solution of iron and manganese in surface waters the iron might, where the conditions are favorable, be precipitated as sulphide (FeS_2) and the manganese might be carried on in solution to be deposited somewhere else as oxide or carbonate. Subsequently the oxidation of the ores would give rise to oxide of iron from the sulphide and oxide of manganese from the carbonate; and the two ores, though occurring at the same horizon, would be separated by a greater or less distance.

After the deposition of the sulphide of iron, the conditions might change and permit the deposition, in the same place, of the carbonates of iron and manganese together. This is an easy case to imagine, and where such a deposit was exposed to surface influences, the resulting product would be oxide of iron from the underlying sulphide and a manganiferous iron oxide from the overlying isomorphous carbonates. Hence another possible cause of the frequent association of pure iron ores and manganiferous iron ores. It is possible also that after the solution of iron and manganese had been freed from the former by precipitation as sulphide, the manganese might be carried on and laid down as carbonate on a previous deposit of iron sulphide, and when such a combination was oxidized, the result would be oxide of iron and oxide of manganese in beds closely associated but yet distinct.

By supposing the iron sometimes to be deposited in sea water as glauconite, a manner in which manganese is not laid down (see page 365), a further means of separation of the two metals would result.

Thus by alternating the conditions of the deposition of iron and manganese in different forms, a great variety of methods of association and separation of the two metals can be produced.

The above discussion refers not only to the deposits of iron and manganese ores of notable size, but also to the iron and man-

ganese frequently found disseminated through shales, sandstones etc. In these rocks they usually form a small but often a very important part, for in many cases the iron and manganese is taken into solution from the rocks and redeposited by a process of replacement with carbonate of lime in neighboring beds of limestone, or more rarely by replacement with other rocks, thus giving rise to important ore deposits. The question of the association and separation of the iron and manganese in these replacement deposits depends on a number of conditions, the principal of which are, just as in the class of deposits that has been discussed, the conditions during deposition and the forms in which the iron and manganese are precipitated. The processes by which association and separation occur in replacement deposits differ somewhat in detail from the processes just discussed, but are based on the same principles.

Many of the iron and manganese deposits of the Appalachian region are supposed by many to be replacement deposits.. N. S. Shaler¹ in 1877 suggested that some of the iron deposits of Kentucky and Ohio were formed by the solution of iron from certain rocks, and its deposition in the form of carbonates by replacement with underlying limestone. Subsequently it was changed by oxidation to brown hematite. A notable case of replacement has also been shown by R. D. Irving and C. R. Van Hise² in the iron deposits of the Penokee series of Michigan and Wisconsin. Here the ore is supposed to be partly a replacement of chert in a trough between quartzite and igneous rocks. The solution that contained the iron was derived from strata in the same series of rocks in which the iron was re-deposited and contained a certain amount of manganese. It is shown how the iron and manganese were more or less separated in the replacement process and that the separation was due to the difference in the oxidability of the carbonates as explained on page 363.

R. A. F. PENROSE, JR.

¹ Kentucky Geol. Survey, Report of Progress, Vol. III., New Series, 1877, p. 164.

² U. S. Geol. Survey, Tenth Annual Report, 1888-1889, Vol. I., pp. 409-422.